

Japanese Kokoku Patent No. Hei 4[1992]-9231

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## METHOD OF RECYCLING OLD PAPER THROUGH BIOCHEMICAL REMOVAL OF INK

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References Cited: Japanese Kokai Patent  
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[There are no amendments to this patent.]

### Claims

1. A biological ink removal method characterized by pulping  
used printing paper with an enzyme within a pH range of 3-8 and

removing the ink particles from the fibers through a flotation and/or washing method.

2. The biological ink removal method described in Claim 1, characterized by using cellulase and/or pectinase as the enzyme.

3. The biological ink removal method described in Claim 1 or 2, characterized by adding the enzyme in an amount of 0.005-5% of the dry weight of the used paper.

4. The biological ink removal method described in Claim 1, characterized by controlling the temperature during the pulping process to within a range from room temperature to 60°C.

#### Detailed explanation of the invention

#### Industrial application field

This invention is concerned with a method to recycle useful pulp fibers from used paper that does or does not contain wood through a biological method in an ink removal process.

Basically, removing ink from pulp fibers is a process in which ink is considered a stain and the stain is either removed or cleaned.

#### Prior art

Chemicals are used together with heat and mechanical energy to remove ink particles from fibers and disperse them into an aqueous medium. The ink particles are then separated from the pulp fibers either by washing or flotation or by using a modern hybridized process in which the said two elements are combined.

The chemical used in the conventional ink removal process is a surfactant, having, as its functions, a washing property to eliminate the ink from the fibers, a dispersing action to maintain the dispersed ink particles in order to prevent their reaccumulation over the fibers, and a floating action for foam flotation of the ink particles.

Typical surfactants are in the form of long chain molecules having a hydrophobic section at one end and a hydrophilic section at the other. The hydrophobic portion may consist of a fatty acid, aliphatic alcohol, alkylphenol, and other oil-soluble surfactants.

The hydrophilic portion in the ink removal surfactant generally consists of anionic molecules, such as carboxylates and sulfonates, and nonionic molecules, such as polyoxyethylenated chains, for example.

Typical surfactants commonly used in the washing and foam flotation ink removal process include: linear fatty acid sodium [salts] as well as potassium salt (soap), linear alkyl benzene sulfonates (LAS), olefin sulfonates, long-chain aliphatic alcohols, polyoxyethylenated alkylphenols, alkylphenol ethoxylates, and polyoxyethylenated linear alcohols.

The major disadvantage of using said surfactants during the ink removal process is an excessive amount of foam formed during the flow of pulp material (stock) and the paper manufacturing process line that follow. Some of the aforementioned surfactants are resistant during biological decomposition at the wastewater treatment stage and bring about serious environmental problems.

A scavenger is added during the foam flotation ink removal process, in order to collect the ink into a large aggregate of

particles, and adhered to the air bubbles. The scavenger is necessary for effective flotation, and it generally is an anionic, long-chain fatty acid soap. The fatty acid scavenger precipitates together with calcium ions and forms large, insoluble ink particles and scavenger particles. The ink particles, in the form of aggregates, are adhered to the bubbles by an injection of air at the cells; they float to the surface and are removed from the system as floating scum.

The major disadvantage in the flotation method using the fatty acid scavenger is the problem of accumulation of pitch and the adherence of calcium to the scale at the raw material line and the paper manufacturing processing device that follow. Chemicals other than the surfactant include: caustic soda, sodium silicate, a metal ion chelating agent, and hydrogen peroxide.

The hydrogen peroxide bleaching agent must be added in order to prevent possible yellowing of the pulp due to the addition of the caustic soda, and to also improve the brightness of the pulp fibers.

Conventional ink removal, which is assisted by a surfactant, encounters serious problems when used with paper printed in ink that is coated in large amounts, is highly polymerized, or is nonimpact, for example, with the use of ultraviolet light, thermosetting, xerox, laser, and ink jets, due to the advancements in modern printing and copying technology. Such inks generally contain hardened polymer resin, which strongly binds the ink particles to the surface of the fibers in a manner so that the ink cannot be removed completely using conventional ink removing chemicals during the defiberizing (pulping) stage of the used paper. An excessive amount of heat and mechanical

energy are also required in addition to the ineffective conventional chemicals.

The main technological problem in the conventional floating ink removal process for used paper, such as newspaper, is related to small ink particles imbedded in bundles of fibers and among small fibers; it is also impossible to remove these particles from the fibers through washing and/or a floating process.

Problem to be solved by this invention

This invention provides a new and further improved ink removal method that can be effectively used for removing ink from newspaper paper, from printed used paper that does not contain wood, such as whiteledger, for example, laser-printed copy paper of the electrostatic photographic method, and computer-printed used paper.

Means for solving the problem

Ink particles are removed in the ink removal method of this invention by utilizing the biological action of enzymes on the surface of cellulose fibers, and also the dispersing function of enzymatic proteins on the ink particles.

Contrary to the conventional method, alkali and ink removing surfactants are not necessary, although some types of surfactants may be used together with the enzyme in order to increase the ink removal efficiency. The fatty acid scavenger is not necessary during the foam flotation process. The hydrogen peroxide bleaching agent, which prevents yellowing, also is not necessary

because caustic soda is not used during the ink removal of the newspaper paper.

The exclusion of the fatty acid scavenger in this biological ink removal process solves the problem of stubborn pitch and scale deposits that accompany the conventional flotation process, in which the fatty acid soap, calcium salt, and silicate are used.

The method in this invention will be explained in detail below.

Newspaper, such as old newspaper for example, or printed used paper that does not contain wood, is dissolved in a common pulper (concentration of 4-7%) or in a highly concentrated pulper (12-15%) with a water temperature of room temperature to 60°C. The amount of enzyme added is 0.005-5.0% based on the dry weight of the used paper, and the pH of the material slurry is adjusted to 3.0-8.0. Compared to the conventional pulping process, which uses caustic soda and a surfactant, the pulping process in this enzyme method is completed in a relatively short time, and the ink particles are completely separated from the surface of the fibers and dispersed sufficiently. The dispersed ink is removed from the pulp fibers by a one-stage or a multistage common washing process device, such as a vibrating strainer and drum washing machine, for example, without the assistance of the surfactant with the washing force. The ink particles, which are dispersed by the action of the enzymatic protein, can also be selectively removed from the diluted pulp slurry by a common flotation device, in which the foam formed by injected and absorbed air in the pulp pick up the particles. The fatty acid scavenger is not necessary with used newspaper paper. However,



with laser-printed used paper, a small amount of the fatty acid scavenger may be added in order to increase the ink removing efficiency.

#### Function

The addition of the enzyme in this biological ink removal process results in a substantial reduction in the pulping time, as compared to pulping without the presence of the enzyme. Therefore, the pulping energy is lowered substantially, e.g., a margin of almost 50% reduction can be achieved. The faster and easier pulping observed using the enzyme may result from the unique biological activity of the enzyme, which is effective in dissolving the binding of the fibers and removing the ink that is bound to the surface of the fibers, the bundles of fibers, or among the small fibers. A partial hydrolysis of cellulose by the enzyme may occur within the microstructure at the surface of the fibers during the pulping stage. Due to said biological activity, the enzyme can remove the small ink particles embedded in the bundles of fibers and within the small fibers and microfibers, which could not be removed previously from old newspaper paper using the conventional ink removal chemicals.

The addition of hydrogen peroxide to prevent yellowing of the fibers is not necessary in this biological ink removal method for old newspaper paper. Accordingly, this brings about a substantial reduction in the cost of ink removal chemicals compared to the conventional ink removal process, which uses caustic soda, hydrogen peroxide, a chelating agent, and sodium silicate.

In addition to the much greater brightness in the pulp formed, it should be noted that the physical strength of the pulp fibers manufactured according to the method of this invention is higher than that of the corresponding pulp manufactured according to the conventional method. The addition of the enzyme appears not to deteriorate the strength of the fibers, but rather it improves the strength of the fibers due to an unknown reason.

#### Application examples

##### Application Example 1

#### Ink removal of old newspaper paper with a cellulose decomposing enzyme

A sample of used old newspaper was added to a pulper. It was then filled with water at 40°C at a concentration of 4%, and cellulose was dissolved at a dosage level of 0.1% based on the oven dry weight of the used paper. This used paper was soaked for 10 min and then disintegrated for 5 min. Half of the pulp slurry was diluted to a concentration of 1% after a complete disintegration of the used paper.

The diluted pulp slurry was transferred to an air flotation cell, and then dispersed ink particles were eliminated from the pulp slurry by removing the ink particle foam from the cell as floating scum by injecting air through a porous plate. The flotation time necessary to remove the ink foam completely was 1 min.

The remaining half of the pulp slurry was washed through an experimental vibrating strainer and the dispersed ink particles were removed.

The generated and recycled pulp fibers obtained through the flotation and washing processes were evaluated with respect to brightness and mechanical strength of the pulp. In order to compare this enzyme-treated, ink-removed pulp with a conventional ink-removed pulp, the same used paper sample was treated in a pulper in which 1.0% NaOH, 0.3% H<sub>2</sub>O<sub>2</sub>, a 3% sodium silicate solution (water glass), 0.8% Serfax MT-90 (fatty acid soap), and 0.2% Igepal-660 were added, based on the oven dry weight of the used paper. The pulping time required for complete disintegration was 10 min. After diluting to a concentration of 1%, the dispersed ink particles were removed by the flotation method at the experimental flotation cell as in the method described above.

As indicated in Table I, the brightness of the pulp in this invention, in which the ink was removed with the enzyme, was much higher than the brightness of the pulp in which the ink was removed using the conventional chemicals and alkali-tolerant cellulase. The mechanical strength of the ink-removed pulp, treated with the enzyme, was also superior to the mechanical strength of the pulp in which the ink was removed by the fatty acid scavenger and the dispersant (Igepal-660). A microscopic observation revealed that the pulp manufactured by this invention, contained longer fiber fragments, had smoother fiber surfaces, and that the mechanical damage was much smaller.

Table I. Comparison of the nature of the pulp recycled by the method in this invention and the conventional method

	① 明るさ (%)		② 引張係数 (N, m/g)		③ 引裂係数 (N, m/g)	
	KNOP	ANOP	KNOP	ANOP	KNOP	ANOP
④ 本発明方法 浮選	47.1	45.2	28.9	32.4	11.7	13.6
⑤ 本発明方法 洗浄	50.3	48.6	29.3	32.9	11.8	14.1
⑥ セルフアックス MT-90	45.1	38.4	30.1	32.8	10.8	13.1
⑦ Alkali 耐性セルラーゼ	35.2	34.4	-	-	-	-
⑧ KNOP: 韓国の古い新聞用紙						
⑨ ANOP: 米国の古い新聞用紙						

Key: 1 Brightness  
 2 Tensile strength  
 3 Tearing strength  
 4 Flotation in the method in this invention  
 5 Washing in the method in this invention  
 6 Serfax MT-90  
 7 Alkali resistant cellulase  
 8 KNOP: Old Korean newspaper paper  
 9 ANOP: Old U.S. newspaper paper

With respect to washing, the enzyme-treated pulp provided cleaner and brighter pulp when compared to floating ink removal [pulp].

The addition of the enzyme appears to substantially accelerate the disintegration of the used paper. When disintegrating old newspaper paper in a common pulper at a concentration of 4%, the addition of a 0.5% enzyme reduced the pulping time from 5 min (without the addition of the enzyme) to 30 sec for a complete disintegration, as indicated in Table II.

Table II. Relationship between the enzyme addition and disintegration time

① 酵素(%)	0.5	0.1	0
② 解体時間(秒)	30>	60-120	300<

Key: 1 Enzyme (%)  
2 Disintegration time (sec)

#### Application Example 2

Removal of laser CPO (computer printout) ink with cellulose decomposing enzyme

It is almost impossible to attain complete elimination of the laser-beam-hardened ink particles from the laser CPO used paper using conventional ink removal chemicals. This is because the ink particles adhere to the surface of the fibers at a strength that does not allow them to be removed and dispersed from the pulp water slurry by the alkali and common ink removal surfactants in the conventional ink removing chemicals.

A sample of laser CPO used paper was added to the water in an experimental, highly concentrated pulper at a concentration of 12.5%, and cellulase was added to said water at a dosage level of 0.2%, based on the dry weight of the paper. Pulping was performed for 20 min at a material water temperature of above 20-35°C. A completely disintegrated pulp slurry was diluted to

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0.5%, and the dispersed ink particles were then eliminated from the pulp slurry using an experimental flotation cell as in the explanation in Application Example 1. In this example, a small amount of a commonly used fatty acid scavenger, 0.3% Serfax MT-90, based on the dry weight of the used paper, was added prior to air flotation in order to increase the removal efficiency and selectivity of the ink, and the flotation time was 3 min. The conventional ink-removed pulp, to be compared to the enzyme ink removed pulp, was manufactured in the same method, except for the different chemical conditions below:

Based on the dry weight of the used paper,

1% NaOH

0.1% Igepal 660 dispersant

0.8% Serfax MT-90

Pulping temperature: 50°C

Pulping time: 30 min

Addition of calcium salt to the flotation cell: 200 ppm

Flotation time: 3 min

The brightnesses and strengths of the pulp samples formed were compared in Table III.

As indicated in this table, the image analysis of the pulp samples indicates that the number of residual ink particles was much more reduced, approximately 10 times, in the pump in which ink was removed with the enzyme, and the tensile strength was also much higher as compared to the pulp manufactured using conventional chemicals.

A high-quality recycled chemical pulp, in terms of the amount of staining and the fiber strength, can be obtained using

an enzyme in combination with a small amount of a fatty acid scavenger in the flotation method.

Table III. Comparison of the recycled pulps in the method in this invention and the conventional method

⑤	① 明るさ	② 汚物量	③ 引張係数
	(%)	(数/面積)	(N. m/g)
酵素+MT-90 (0.5%)	79.0	450	34.3
MT-90(90%)	80.6	4330	26.3

Key: 1    Brightness  
 2    Amount of staining  
 3    Tensile strength  
 4    (Number/area)  
 5    Enzyme + MT-90

### Application Example 3

Ink removal from used newspaper paper with a pectinolytic enzyme

Used newspaper paper containing 0.1% pectinase was soaked for 10 min at 40°C in a method identical to that in Application Example 1 and was disintegrated for 5 min. The disintegrated pulp was diluted to 1%, and the ink particles were removed for 1 min through flotation.

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As indicated in Table IV, the brightness and tensile strength of a paper sheet manufactured by the method in this invention improved.

Table IV. Comparison of the method using the pectinolytic enzyme and the conventional method

	① 明るさ (%)	② 引張係数 (N.m/g)
③ 本方法	44.2	33.3
MT-90(0.8%)	38.4	32.8

Key: 1      Brightness  
       2      Tensile strength  
       3      The method of this invention





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